Low-Density Polymer Thin Film Formation in Supercritical Carbon Dioxide

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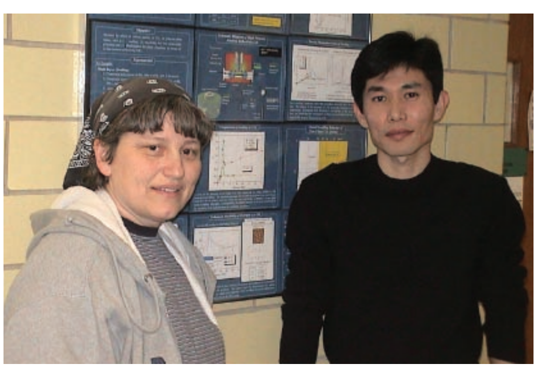
We have developed a method for producing stable low-density polymer films using supercritical carbon dioxide (scCO$_2$). Two different molecular-weight polystyrene films with various thicknesses were exposed to scCO$_2$ along the density fluctuation ridge in a phase diagram. The swollen structures could be then frozen via the flash evaporation of CO$_2$ without forming additional large voids. X-ray reflectivity data clearly showed that exposure to scCO$_2$ could be used to produce uniform low-density films about 2R$_g$ thick or less, where R$_g$ is the radius of polymer gyration.

Increased miniaturization in the electronics industry has produced a need for highly uniform ultrathin polymer coatings with well-controlled optical and dielectric properties. Often the thickness of these films is commensurate with a few radii of gyration (R$_g$) of the polymer, and tight clearances impose very strict tolerances on surface roughness. This high degree of confinement therefore makes it difficult to satisfy the stringent uniformity requirements if we modify the electronic properties using standard gas foaming methods or blending it with other polymers or inorganic additives. Here we show a novel approach for producing stable, uniform, low-density polymer films using supercritical carbon dioxide (scCO$_2$).

ScCO$_2$ has long been known to be a "green" medium for polymer chemistry or material science. Unfortunately, its potential benefits have not been fully exploited since only a limited class of polymers can be dissolved in it. Recently, we have shown that a wide variety of polymer thin films can swell by as much as 30 to 60% when exposed to scCO$_2$ within a narrow temperature and pressure regime, known as the "density fluctuation ridge," even when the bulk miscibility of the films with scCO$_2$ is poor. In addition, we found that the *in situ* film quality, i.e. density, roughness, and film thickness, could be frozen via the flash evaporation of CO$_2$. We report x-ray reflectivity measurements in which the density profile of the vitrified films is measured directly and correlated with other properties, such as the dielectric constant, index of refraction, and surface glass transition.

Two kinds of polystyrene (PS), corresponding to molecular weights (M$_w$) of 2.0×10^5 and 6.5×10^5 g/mol, were used in this study. Thin films spun cast on cleaned Si substrates were placed in a high-pressure chamber containing scCO$_2$ at T = 36°C and P = 8.2 MPa, i.e. the ridge condition, for two hours and then quickly depressurized to atmospheric pressure within 10 seconds. The films were then characterized by x-ray reflectivity at beamline X10B. As shown in **Figure 1**, we found that the density of the films, which is obtained from a



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dispersion value in the x-ray refractive index, decreased from 23% to 13% by varying the thickness of both PS films. Furthermore, the data could be collapsed on a universal curve when the initial film thickness (L_0) was scaled by R_g (**Figure 1** inset). Hence, when confined as a thin film on a surface, thickness and molecular structure influence the density of the materials.

The reduction in density has several consequences affecting the material properties of the films. First, there is a decrease in its optical index of refraction (or dielectric constant). **Figure 2** shows the refractive indices (n_f) of the PS (M_w = 6.5×10^5 g/mol) films for the unexposed and two exposed films measured using spectroscopic ellipsometry. From the figure we can clearly see that the n_f values for the exposed films decreased with decreasing L_o values over the wide wavelength range. Second, there is a decrease in the glass transition temperature (T_g). In the **Figure 2** inset, we plot the modulation amplitude vs. T for unexposed and exposed PS thin films obtained using the Shear Modulation Force Microscopy technique. From the figure we can see that the discontinuity in the plot, which corresponds to T_g, occurs at T = 100ºC for the unexposed film. The T_g value for the exposed film decreases by 10ºC compared to that of the unexposed PS film.

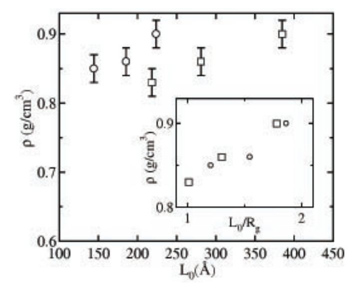

Figure 1. Density (ρ) vs. L_0 for the exposed films: PS (M_w = 2.0×10^5) (o), PS (M_w=6.5×10^5) (□). In the inset, L_0/R_g dependence of ρ is shown.

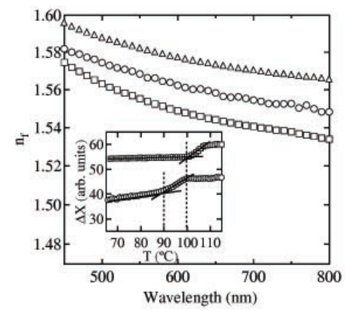

Figure 2. Index of refraction for PS (M_w = 6.5×10^5): before (Δ) and after (L_0 = $2R_g$ (o) and L_0 = $1.3R_g$ (□)). In the inset, X vs. T curves for PS films: exposed films L_0=$1.3R_g$ (o) and unexposed film (□).